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Modelling of Polymer Photodegradation

for Solar Cell Modules

A Quarterly Technical Progress Report

Covering the Period April 1 - June 30, 1983

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LSA Project, Technology Development Area

Contract Goals and Objectives

As part of the Encapsulation Task, this research program is intended to model the photodegradation of synthetic polymers used as pottants and/or cover sheets in the LSA solar cell module designs. It involves the development of a computer simulation of the chemical processes that take place under weathering conditions which could, in principle, relate directly to the performance of these materials and afford some basis for predicting and/or controlling their useful lifetimes.

The program can be divided into three main parts:

1. The development of a computer program to model the weathering/ photooxidation of an ethylene-vinyl acetate copolymer as a typical candidate for LSA applications.
2. The development of new analytical procedures for the determination of photooxidation and photodegradation at early stages in solid polymer samples.
3. The development of weathering tests suitable for use with a computer kinetic model to provide a basis for extrapolated predictions.

Summary

We have already shown that many of the experimental observations in the photooxidation of hydrocarbon polymers can be accounted for with a computer simulation using a mechanistic model with corresponding rate constants for each elementary reaction. However, it is obvious that in outdoor applications, such as with photovoltaic modules, the variation of temperature will have important effects on the useful lifetimes of such materials.

In the last quarter we have eventually managed to model the photooxidation process with input data consisting of Arrhenius parameters A (the pre-exponential factor) and E (the activation energy). This naturally multiplied the mathematical complexity in the program but moreso, the different magnitudes of the activation energy caused various changes in the relative importance of the various key processes of propagation and termination with changes in temperature.

We have also now included the thermal reactions of hydroperoxide decomposition:

$$ROOH \xrightarrow{\Delta} RO\cdot + OH\cdot$$

This increased the reaction basis set from 51 to 56 reactions. The complete and revised data base is summarised in Table I.

Figure 1 shows the variation of time to failure (5% oxidation, as before) with temperature. The decrease in lifetime (no stabiliser) is, more or less, as expected. The change in temperature from 280 K (45 °F, a cool tropical day) to 310 K (100 °F, a hot tropical day) shortens the time to failure from 20 months to three months. An attempt at a typical Arrhenius plot (Fig. 2) shows an "apparent net activation energy" of 10 kcal/mole.

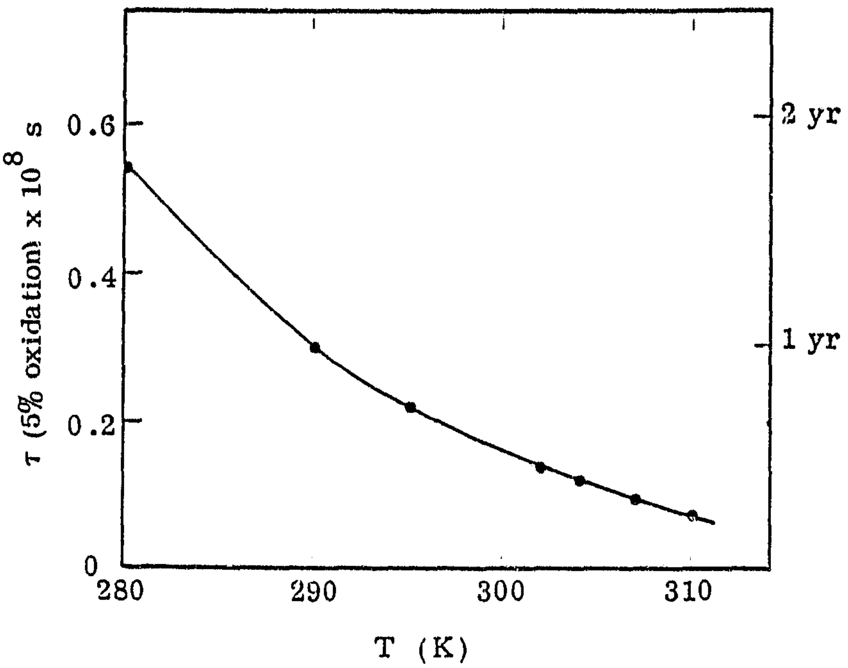

FIGURE 1. Time to failure (5% oxidation) as a function of temperature.

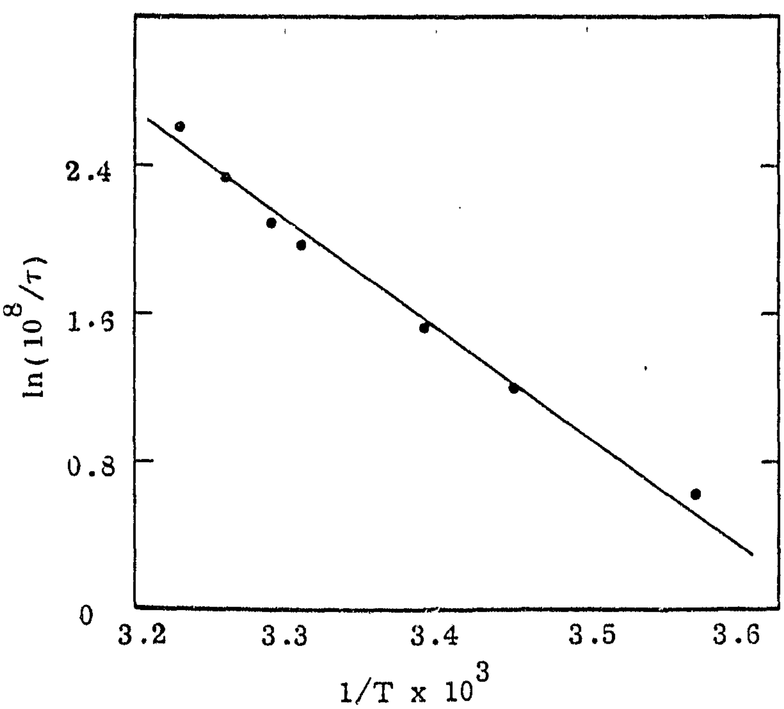

FIGURE 2. Arrhenius plot of the rate of oxidation (k vs. 1/T).

TABLE I. Data Set: Photooxidation Reaction Scheme and Activation Parameters

	Reaction matrix			A	E kcal/mol
1.	Ketone	⟶	KET*	0.70×10^{-9}	0
2.	KET*	⟶	$SMRO_2$ + SMRCO	0.59×10^{9}	4.8
3.	SMRCO	⟶	$SMRO_2$ + CO	0.80×10^{17}	15
4.	KET*	⟶	Alkene + SMKetone	0.56×10^{8}	2.0
5.	SMKetone	⟶	SMKET*	0.70×10^{-9}	0
6.	SMKET*	⟶	$SMRO_2$ + CH_3CO	0.32×10^{13}	8.5
7.	SMKET*	⟶	Alkene + Acetone	0.56×10^{9}	2.0
8.	ROOH	⟶	RO + OH	0.13×10^{9}	0
9.	RO_2 + RH	⟶	ROOH + RO_2	0.10×10^{10}	17.0
10.	$SMRO_2$ + RH	⟶	SMROOH + RO_2	0.10×10^{10}	17.0
11.	SMROOH	⟶	SMRO + OH	0.13×10^{-9}	0
12	SMRO + RH	⟶	SMROH + RO_2	0.16×10^{10}	6.2
13.	RO + RH	⟶	ROH + RO_2	0.16×10^{10}	6.2
14.	RO	⟶	$SMRO_2$ + Aldehyde	0.32×10^{16}	17.4
15.	KET* + ROOH	⟶	Ketone + RO + OH	0.25×10^{10}	11.6
16.	SMKET* + ROOH	⟶	SMKetone + RO + OH	0.25×10^{10}	11.6
17.	SMRCO + O_2	⟶	SMRCOOO	0.80×10^{14}	9.6
18.	SMRCO + RH	⟶	RO_2 + Aldehyde	0.10×10^{10}	7.3
19.	SMRCOOO + RH	⟶	SMRCOOOH + RO_2	0.10×10^{10}	17.0
20.	SMRCOOOH	⟶	SMRCOO + OH	0.13×10^{-9}	0
21.	SMRCOO	⟶	$SMRO_2$ + CO_2	0.10×10^{15}	6.6

22.	SMRCOO + RH	⟶	Acid + RO_2	0.10×10^{10}	17.0
23.	OH + RH	⟶	RO_2 + Water	0.10×10^{10}	0.5
24.	CH_3CO + RH	⟶	RO_2 + CH_3CHO	0.10×10^{10}	7.3
25.	CH_3CO + O_2	⟶	CH_3COOO	0.89×10^{14}	9.6
26.	CH_3COOO + RH	⟶	CH_3COOOH + RO_2	0.10×10^{10}	17.0
27.	CH_3COOOH	⟶	CH_3COO + OH	0.13×10^{-9}	0
28.	CH_3COO + RH	⟶	CH_3COOH + RO_2	0.10×10^{15}	6.6
29.	KET*	⟶	Ketone	0.10×10^{9}	0
30.	SMKET*	⟶	SMKetone	0.10×10^{9}	0
31.	KET* + O_2	⟶	Ketone + SO_2	0.89×10^{14}	9.6
32.	SMKET* + O_2	⟶	SMKetone + SO_2	0.89×10^{14}	9.6
33.	RO_2 + RO_2	⟶	ROH + Ketone + SO_2	0.25×10^{10}	11.6
34.	RO_2 + ROH	⟶	ROOH + Ketone + HOO	0.10×10^{10}	15.3
35.	HOO + RH	⟶	HOOH + RO_2	0.32×10^{9}	15.0
36.	HOO + RO_2	⟶	ROOH + SO_2	0.32×10^{9}	2.1
37.	RO_2 + Ketone	⟶	ROOH + Peroxy CO	0.13×10^{5}	8.9
38.	Peroxy CO + RH	⟶	PER OOH + RO_2	0.10×10^{10}	17.0
39.	PER OOH	⟶	PER O + OH	0.13×10^{-9}	0
40.	PER O + RO_2	⟶	DIKetone + ROOH	0.25×10^{10}	11.6
41.	RO_2 + ROOH	⟶	ROOH + Ketone + OH	0.25×10^{8}	11.6
42.	RO_2 + SMROH	⟶	ROOH + Aldehyde + HOO	0.10×10^{10}	15.3
43.	RO_2 + Aldehyde	⟶	ROOH + SMRCO	0.25×10^{10}	11.6
44.	RO_2 + RO_2	⟶	ROOR + SO_2	0.38×10^{12}	16.0

45.	SO_2	$\longrightarrow$	O_2	0.63×10^{5}	0
46.	SO_2 + Alkene	$\longrightarrow$	ROOH	0.20×10^{14}	10.0
47.	RO_2 + Alkene	$\longrightarrow$	Branch	0.16×10^{9}	11.6
48.	$SMRO_2$ + Alkene	$\longrightarrow$	ROOH	0.16×10^{9}	11.6
49.	RO_2 + QH	$\longrightarrow$	ROOH + Q	0.16×10^{8}	5.2
50.	KET* + Q1	$\longrightarrow$	Ketone + Heat	0.80×10^{13}	9.5
51.	ROOH + QD	$\longrightarrow$	PRODS	0.80×10^{13}	9.5
52.	ROOH	$\longrightarrow$	RO· + OH·	0.63×10^{15}	35
53.	SMROOH	$\longrightarrow$	SMRO + OH	0.63×10^{15}	35
54.	SMRCOOOH	$\longrightarrow$	SMRCOO + OH	0.63×10^{15}	35
55.	CH_3COOOH	$\longrightarrow$	CH_3COO + OH	0.63×10^{15}	35
56.	PEROOH	$\longrightarrow$	PERO + OH	0.63×10^{15}	35